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ACTIVATION PARAMETERS OF FLOW THROUGH BATTERY SEPARATORS

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SUMMARY

Studies of the hydrodynamic flow of water and 45 percent potassium hydroxide (KOH) solution through a microporous and an ion-exchange separator are described. The permeability values are interpreted in terms of a pseudo-activation process. The enthalpy of activation, ΔH^* , and the entropy of activation, ΔS^* , have been estimated from Eyring's rate equation.

INTRODUCTION

The performance of most electrochemical devices has been largely attributed to the proper functioning of the separators. During operation of these devices, the electrolyte components move from one electrode compartment to another through the separators. This flow depends on the selective characteristics of the separator arising from porosity, the hydrophilic or hydrophobic character, and the charge density of the separator.

The hydrodynamic flow of a fluid through a porous medium can be either viscous flow or diffusional flow or a combination of the two as characterized by irreversible thermodynamics. If there is a gradient of chemical potential across the separator, the overall flow will be dominated by the diffusional flow, and if there is a pressure difference (developed due to evolution of gases at the electrodes or to electro-osmosis), the flow will be viscous flow. Further, during charging and discharging of the battery, temperature fluctuations occur, and these flows vary exponentially (ref. 1) with temperature. The dependence of these flows on temperature is characterized in terms of the activation energy (ref. 2). The present study determined activation parameters for the hydrodynamic flow of water and 45 percent KOH solution through a microporous separator (viz, fuel cell grade asbestos (FCGA) having 5 percent butyl latex rubber (EBL) as binder supplied by Quinn-T. Co., New Hampshire) and an ion-exchange separator (viz, P2193, 40/60 supplied by RAI Research Corporation, New York).

EXPERIMENTAL PROCEDURE

Materials

Certified 45 percent KOH solution (Fisher Scientific) and deionized water (conductivity $\sim 10^6 \text{ ohm}^{-1} \text{ cm}^{-1}$) were used.

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Apparatus

The apparatus consisted of two half-cells made of Plexiglass. Each half-cell had a volume of about 10 milliliters and 0.635-centimeter stainless steel fittings for connections to a pressure head. A glass capillary of 1 millimeter internal diameter was used for determining the rate of flow. The half-cells are clamped against the separator. When studying the FCGA + 5 percent EBL separator, pressure was applied by raising or lowering the pressure chamber. In the case of the P2193, 40/60 separator, pressure was applied with nitrogen gas. The studies with 45 percent KOH solution were performed in a nitrogen atmosphere, and contact with the ambient atmosphere was avoided by using guard tubes and intermediate chambers of KOH pellets.

The separator was fixed between the two half-cells with neoprene rubber gaskets on both sides, and RTV102 cement was used for sealing. Because leakage was the major problem when studies were performed with 45 percent KOH solution, 3.0 psi pressure of nitrogen gas was applied on the inlet side of the cell placed in the water bath. Absence of evolution of gas bubbles in the water surrounding the cell was chosen as the criterion for proper sealing. A stainless steel screen was used as the support for the ion-exchange membrane and a polyethylene screen for the microporous separator. All experiments were performed in a water bath where temperatures could be controlled to within $\pm 0.05^\circ \text{C}$. The capillary height readings were recorded with a traveling microscope having a resolution of 0.001 centimeter. In the case of the microporous separator, the flow was fast, and the time required for 5 centimeters of flow in the capillary was recorded with a stopwatch having a resolution of 0.02 second.

RESULTS AND DISCUSSION

The dissipation function ϕ (ref. 3) for the transport process of liquids through a membrane under the influence of a pressure difference ΔP and concentration difference ΔC can be written as

$$\phi = J_V \cdot \Delta P + J_D \cdot \Delta \pi \quad (1)$$

where J_V is the volume flow, J_D is the diffusional flow, ΔP is the pressure difference, and $\Delta \pi$ is the difference in osmotic pressure across the membrane and is equal to $RT\Delta C$. The phenomenological equations (refs. 3 and 4) relating the flows and forces given in equation (1) are

$$J_V = L_P \cdot \Delta P + L_{PD} \cdot RT\Delta C \quad (2)$$

$$J_D = L_{DP} \cdot \Delta P + L_D \cdot RT\Delta C \quad (3)$$

For such a system, Onsager's reciprocal relation (refs. 5 and 6) is

$$L_{PD} = L_{DP} \quad (4)$$

where L_P and L_D are the mechanical coefficient of filtration (commonly called the permeability coefficient), and the diffusion coefficient, respectively.

Let us consider the experiment in which the concentration of the solute is the same on both sides of the membrane, so that $\Delta\pi$, if any, is zero. Now, if a pressure difference is maintained across the membrane, there exists a volume flow J_v . When the concentration is the same on both sides of the membrane, the volume flow J_v can be given as

$$J_v = L_p \Delta P \quad (5)$$

The values of L_p are estimated from the J_v and ΔP values. The values of J_v , ΔP , and L_p for water and 45 percent KOH solution through the separators at different temperatures are given in tables I and II. The plots of J_v as a function of ΔP for permeation of water through FCGA + 5 percent EBL are shown in figures 1 to 4. The L_p values of microporous separators have an uncertainty of 3.5 percent and ion-exchange separators an uncertainty of 1.2 percent.

Tables I and II show that the permeability of the microporous separator L_p is five orders of magnitude larger than that of the ion-exchange separator. This is not unexpected because the microporous separator has larger pores. The permeability is equivalent to the fluidity of the liquid, and the viscosity is the reciprocal of the fluidity (ref. 2). In general, it is more common to refer to permeability, the tendency to flow, rather than viscosity, the resistance to flow.

In the case of the microporous separator, the permeability is larger with water, and this may be explained as follows: In the absence of electrolyte, the thickness of the electrical double layer in the pores is small enough not to affect the effective pore diameter. As the electrolyte concentration increases, the thickness of the double layer increases, and the effective pore size decreases, thus decreasing the permeability of 45 percent KOH solution. In the case of the ion-exchange separator, the permeability is smaller with KOH solution than with water. This may be attributed to the swelling characteristics of the separator. In the absence of electrolyte the polymeric ion-exchange membrane may be highly swollen. As the electrolyte concentration increases, the membrane may shrink, thus making the effective pore size smaller and decreasing the permeability.

The compatibility of equation (5) with Poissuille's law requires (refs. 7 and 8) that

$$L_p = \pi \sum_{i=1}^{i=n} \frac{r_i^4}{8\eta l} \quad (6)$$

where r_i represents the radii of the i th capillary, n is the number of capillaries or pores in the separator, η is the viscosity of the permeant, and l is the thickness of the separator. The replacement of a single capillary or pore by a porous separator is not expected to change the basic form of the equation (ref. 8). The variation of the viscosity η of a liquid with temperature can be expressed as an activation process:

$$\eta = A e^{E_n/RT} \quad (7)$$

where A and E_n are constants, E_n being the activation energy (ref. 1) per mole for the flow; R is the gas constant; and T is the temperature in Kelvin. Substitution of equation (7) into (6) and taking the logarithm yield

$$\log L_p = K - \frac{E_\eta}{RT} \quad \text{OF PORE QUALITY} \quad (8)$$

where

$$K = \log \pi \sum_{i=1}^{i=n} \frac{\gamma_i}{8TA} = \text{constant}$$

When $\log L_p$ is plotted as a function of $1/T$, a straight line is obtained. This is shown in figures 5 to 8. The values of E_η estimated from the plots are given in table III.

Identifying E_η^* with the enthalpy of activation for viscous flow ΔH^* and using the Eyring rate equation result in

$$\eta = \frac{Nh}{V} \exp\left(\frac{-\Delta S^*}{R}\right) \exp\left(\frac{\Delta H^*}{RT}\right) \quad (9)$$

where η is viscosity of the permeant, N is Avogadro's number, h is Planck's constant, V is the molar volume of the permeant, and ΔS^* is the entropy of activation. The entropy of activation ΔS^* of flow through the separator was estimated by using η values for water and 45 percent KOH and solution from the literature (ref. 8), using values for the constants N and R , and taking V as 18.0 and 12.5 for water and KOH solution, respectively. These values of ΔS^* are given with ΔH^* in table IV.

The negative value of the entropy of activation indicates (ref. 10) that the water molecules were confined to states of high order as they were transformed across the microporous separator. This may be attributed to the hydrophilic nature of the separator. Water enters into electrostatic interaction with the chemical components of the walls of the pores of the separator, and consequently a state of high order is attained. With the KOH solution, the smaller magnitude of ΔS^* may be attributed to the competition between the water molecules bonding with the separator material and the solution ions due to hydration. The positive value of ΔS^* for the ion-exchange separator suggests the absence of electrostatic interactions as the permeant molecules are transferred across the separator.

CONCLUDING REMARKS

The study shows that there is a large difference in the activation parameters for the transport of liquids through microporous and ion-exchange separators. The enthalpy of activation and entropy of activation of transport are useful properties for characterizing different battery separators.

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TABLE I. - PERMEABILITY DATA FOR WATER AND 45 PERCENT KOH
SOLUTION ACROSS MICROPOROUS SEPARATOR

(a) Permeant, water

Temperature, °C	Pressure difference, ΔP , cm of water	Volume flow, J_v , cm ³ sec ⁻¹	Permeability coefficient, L_p , cm ³ sec ⁻¹ atm ⁻¹
25	4.00 3.50 3.25 3.00	3.00x10 ⁻² 2.82 2.33 2.20	7.44
40	4.00 3.50 3.00 2.50	5.00x10 ⁻² 4.68 3.82 2.87	13.02
45	3.75 3.50 3.00 2.25	6.03x10 ⁻² 5.56 4.75 3.65	16.54
50	4.00 3.50 3.00 2.50	6.68x10 ⁻² 5.80 4.85 3.90	16.93

(b) Permeant, 45 percent KOH solution; pressure,
2 centimeter height of solution

Temperature, °C	Volume flow, J_v , cm ³ sec ⁻¹ (a)	Permeability coefficient, L_p , cm ³ sec ⁻¹ atm ⁻¹
24	2.60x10 ⁻⁴	0.135
30	3.33	.172
35	4.18	.216
40	5.33	.275

^aValues represent averages of six or more readings. Flow rate was estimated from time required for liquid meniscus to flow a fixed distance under 2 cm of KOH solution pressure.

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TABLE II. - PERMEABILITY DATA FOR WATER AND 45 PERCENT
KOH SOLUTION ACROSS ION-EXCHANGE SEPARATOR

(a) Permeant, water; pressure, 3.0 psi of nitrogen gas

Temperature, °C	Volume flow, J_v , $\text{cm}^3 \text{ sec}^{-1}$	Permeability coefficient, L_p , $\text{cm}^3 \text{ sec}^{-1} \text{ atm}^{-1}$
22	1.04×10^{-7}	0.51×10^{-6}
30	3.49	1.71
40	6.01	2.94
50	8.94	4.38

(b) Permeant, 45 percent KOH solution

Temperature, °C	Volume flow, J_v , $\text{cm}^3 \text{ sec}^{-1}$	Permeability coefficient, L_p , $\text{cm}^3 \text{ sec}^{-1} \text{ atm}^{-1}$
20	0.79×10^{-7}	0.39×10^{-6}
30	1.39	.68
40	4.06	1.99
50	8.11	3.97

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TABLE III. - ACTIVATION ENERGY OF FLOW THROUGH SEPARATORS

Separator	Permeant	Activation energy, kcal mol ⁻¹
Microporous	Water	1.59±0.08
	KOH solution	3.39±0.10
Ion-exchange	Water	7.78±0.05
	KOH solution	6.47±0.05

TABLE IV. - ACTIVATION PARAMETERS OF FLOW THROUGH SEPARATORS

Separator	Permeant	Enthalpy, ΔH^* , kcal mol ⁻¹	Entropy, ΔS^* , cal deg ⁻¹ mol ⁻¹
Microporous	Water	1.59±0.08	-11.77±0.60
	KOH solution	3.39±0.10	- 6.77±0.20
Ion-exchange	Water	7.78±0.05	9.35±0.08
	KOH solution	6.47±0.05	3.75±0.09

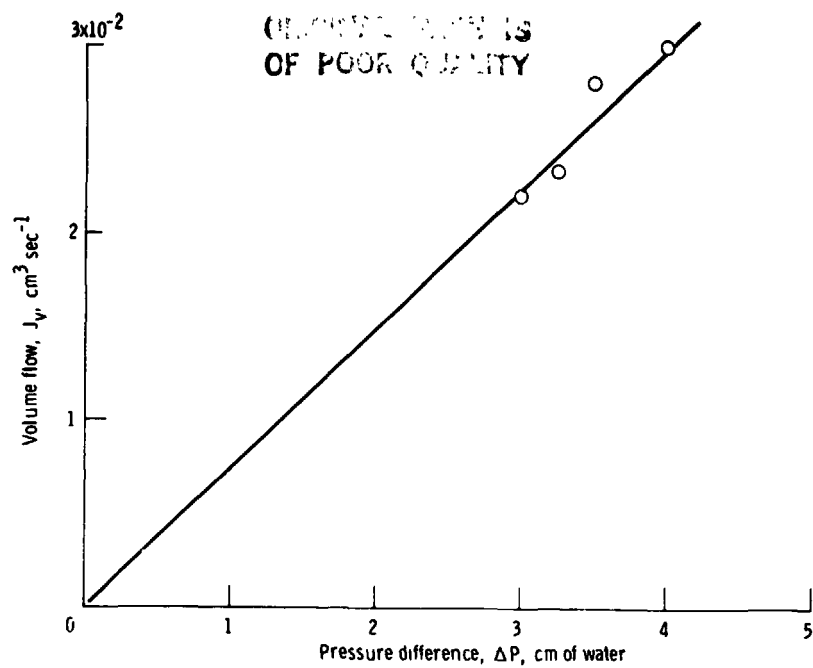


Figure 1. - Volume flow as function of pressure difference for microporous separator at 25° C.

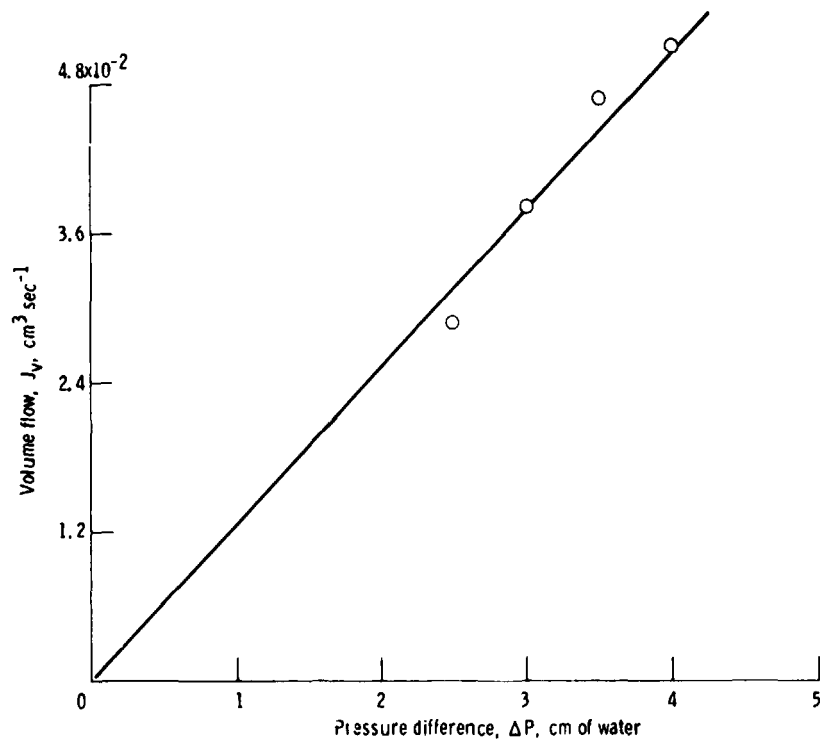


Figure 2. - Volume flow as function of pressure difference for microporous separator at 40° C.

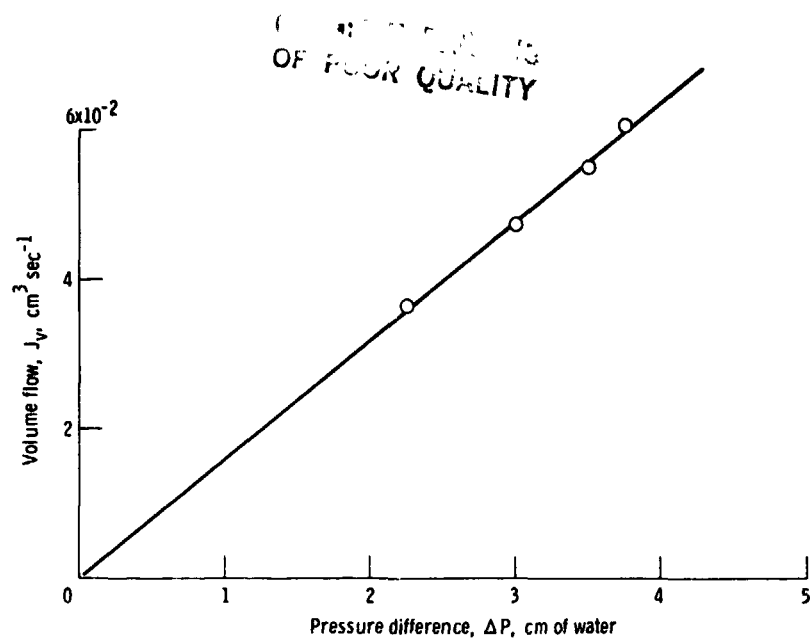


Figure 3. - Volume flow as function of pressure difference for microporous separator at 45° C.

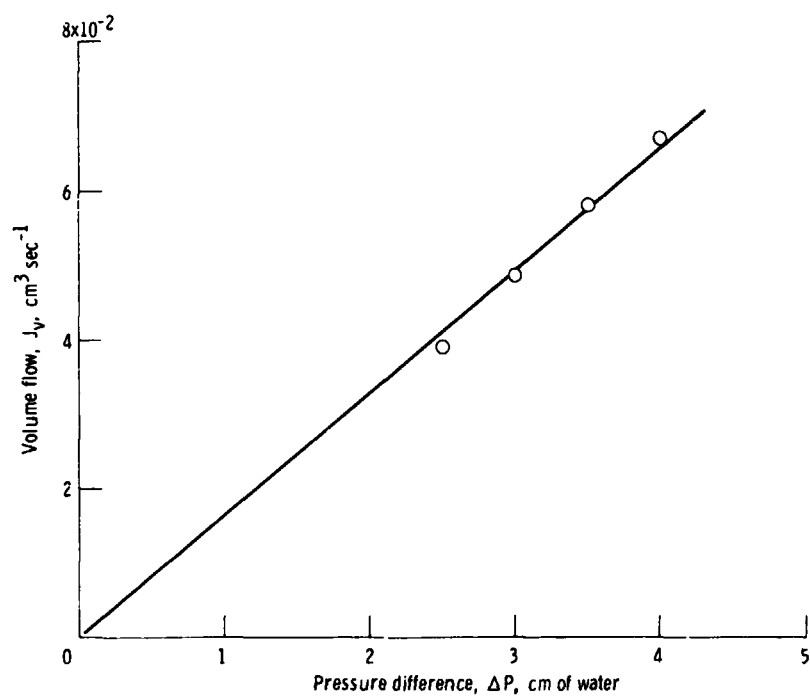


Figure 4. - Volume flow as function of pressure difference for microporous separator at 50° C.

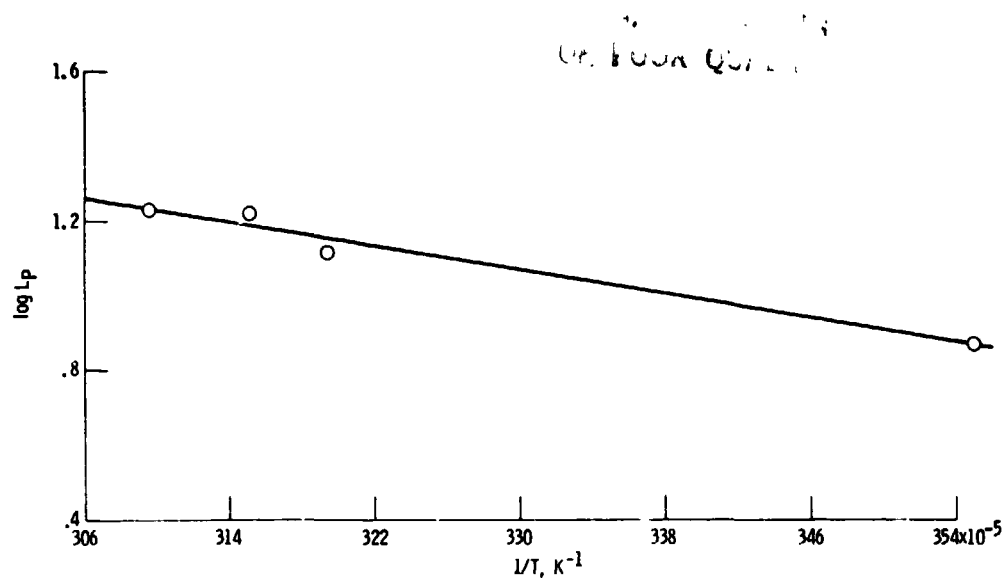


Figure 5. - Arrhenius plot for flow of water through microporous separator.

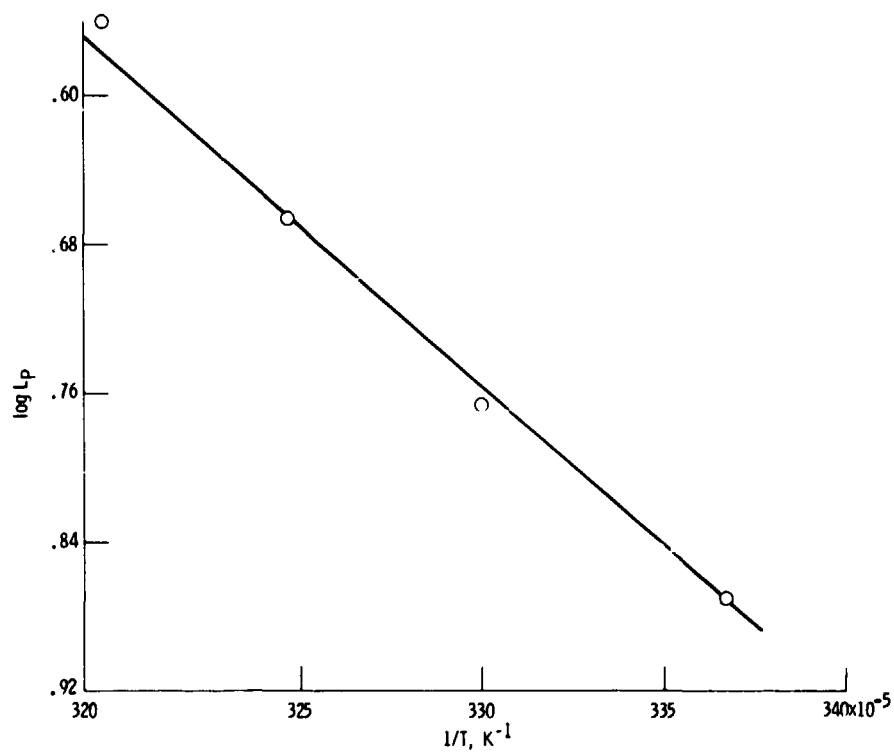


Figure 6. - Arrhenius plot for flow of 45 percent KOH solution through microporous separator.

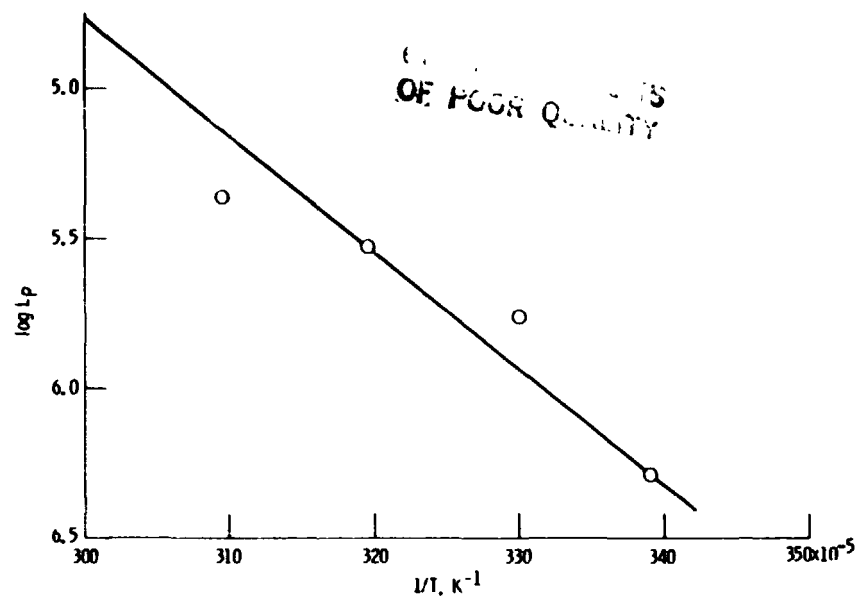


Figure 7. - Arrhenius plot for flow of water through ion-exchange separator.

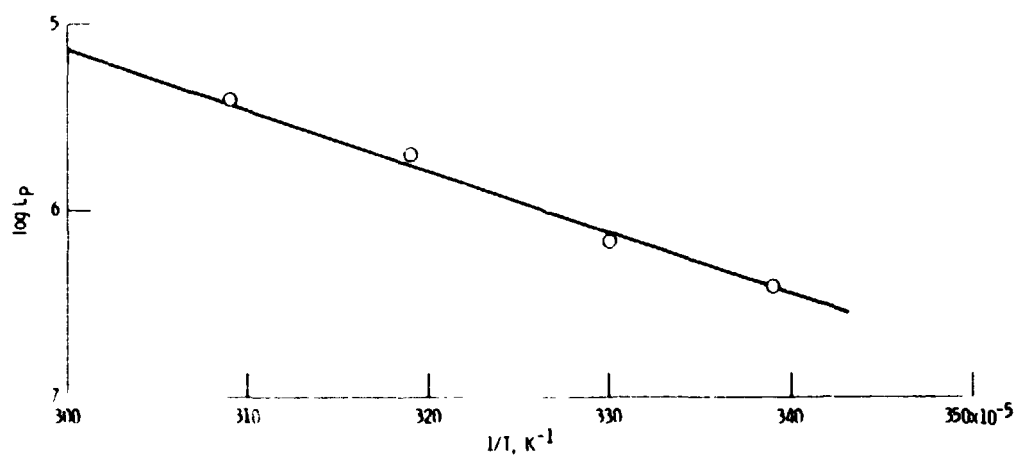


Figure 8. - Arrhenius plot for flow of 45 percent KOH solution through ion-exchange separator.